

GL04023

Cole, D.R., Ohmoto, H. and Lasaga, A.C. (in review) Stable isotopic exchange in mineral-fluid systems. I. Theoretical evaluation of oxygen isotopic exchange accompanying surface exchange and diffusion (submitted to Geochim. Cosmochim. Acta).

Isotopic exchange in mineral-fluid systems.  
I. Theoretical evaluation of oxygen isotopic  
exchange accompanying surface reactions  
and diffusion

D. R. Cole, H. Ohmoto and A. Lasaga  
Dept. of Geosciences, The Pennsylvania  
State University, University Park, Pa.

submitted to Geochim. Cosmochim. Acta

To be submitted to the Geological Society of America Annual Meeting in Cincinnati, held November 2-5, 1981.

ISOTOPIC EXCHANGE IN MINERAL-FLUID SYSTEMS: I. SURFACE EXCHANGE VERSUS DIFFUSION

COLE, David R., Univ. Utah Research Inst., Salt Lake City, Utah 84108; OHMOTO, Hiroshi and LASAGA, Antonio C., Dept. Geosciences, The Pennsylvania State University, University Park, PA 16802

Isotopic exchange between minerals and fluids has been attributed to one of two major processes, precipitation or diffusion. We have developed a model for isotopic reaction kinetics that is consistent with a surface exchange mechanism. The rate equation derived indicates that the rate of isotopic exchange is proportional to the degree of isotopic equilibrium and the product of the number of moles of oxygen (hydrogen) in solution and mineral, and inversely proportional to the surface area of the mineral, the total number of moles of oxygen (hydrogen) in the system and time. Estimates of isotopic rate constants are made for a variety of experimental mineral-fluid systems (e.g., feldspars, calcite, quartz) where precipitation reactions were observed. Oxygen isotopic rate constants computed for these experiments fall between  $10^{-10}$  and  $10^{-5}$  moles  $m^{-2}sec^{-1}$ , with activation energies ranging from 8 to 22  $Kcalmole^{-1}$ . Equations are also given for various grain geometries that relate the diffusion coefficient, grain size, fluid/mineral volume ratio and time to the fraction of isotopic exchange resulting from diffusion of a solute into a solid. By rearranging the surface exchange rate equation, the fraction of isotopic exchange can also be solved as a function of grain size, grain density, fluid/mineral mass ratio, temperature and time. Calculations using these equations indicate that the time required to reach isotopic equilibrium increases with an increase in the fluid/mineral mass ratio and/or grain size and a decrease in temperature, regardless of the mechanism. Isotopic exchange during diffusion, however, is generally four or more orders of magnitude slower. By knowing the mechanism of exchange, it is possible to estimate the times of mineral-fluid interaction for a variety of geologic environments (e.g., diagenetic, ore deposits, metamorphic) that exhibit isotopic disequilibrium.

## Abstract

A rate equation for isotopic (oxygen, hydrogen) exchange between minerals and water has been derived based on a model of removal of atoms from the surface of the solid. Rate constants ( $\text{moles m}^{-2} \text{sec}^{-1}$ ) for oxygen isotopic exchange accompanying surface reactions (dissolution, precipitation) in mineral-fluid systems are obtained from the rate equation

$$r = -\ln(1-F)(WS)/(W+S)(t)(A)$$

where  $W$  and  $S$  are the moles of oxygen in the solution and solid, respectively,  $A$  is the surface area of the mineral ( $\text{m}^2$ ),  $t$  is time (sec) and  $F$  is the degree of equilibrium. Typical rate constants for oxygen isotopic exchange between common silicates (feldspars, quartz, micas) or carbonates (calcite, dolomite) and solutions plot between  $10^{-4}$  and  $10^{-8} \text{ moles m}^{-2} \text{sec}^{-1}$ , with activation energies ranging from 8 to 22  $\text{Kcal mole}^{-1}$ .

These rate constants for surface exchange are used to compute the times required to attain 90% exchange for systems with varying grain radii, mineral/fluid mass ratios, and temperatures. The results of these calculations are compared with times computed from diffusion equations. This comparison indicates that the time required to reach isotopic equilibrium increases with an increase in the fluid/mineral mass ratio and/or grain size, and a decrease in temperature, regardless of the mechanism. Diffusion-controlled oxygen isotopic exchange, however, is several orders of magnitude slower than isotopic exchange accompanying surface reactions.

## INTRODUCTION

The isotopic ratios of  $^{18}\text{O}/^{16}\text{O}$  and D/H have been increasingly used as tracer materials to resolve reaction paths of mineral-fluid reactions occurring both in the laboratory and in nature. Isotopic exchange between minerals and fluids has been attributed to one of two major processes, dissolution-reprecipitation or diffusion. Of these two mechanisms, diffusion of oxygen or oxygen-bearing species such as  $\text{H}_2\text{O}$  or  $\text{OH}^-$  in silicates has received the most attention in recent years. Diffusion coefficients for oxygen (or oxygen-bearing species) have been determined for a variety of mineral-fluid systems, including feldspars (Merigoux, 1968; Anderson and Kasper, 1975; Yund and Anderson, 1974, 1978; Gilletti *et al.*, 1978), phlogopite (Gilletti and Anderson, 1975) and magnetite (Castle and Surman, 1969). These studies have demonstrated that when minerals and fluids are in chemical equilibrium, oxygen isotopic exchange can only occur through a diffusional mechanism.

In contrast, isotopic exchange in mineral-fluid systems that are far from chemical equilibrium is controlled by solution-redeposition. Experimental reactions between high-temperature chloride solutions and feldspars studied by O'Neil and Taylor (1967) and Merigoux (1968) indicate that Na-K ion exchange is always accompanied by oxygen isotopic exchange. O'Neil and Taylor (1967) identified the mechanism of this exchange as a fine-scale recrystallization involving a reaction front moving through the crystal with local dissolution and redeposition in a fluid film at the interface between the exchanged

and unexchanged feldspar. The electron microprobe data from their experiments indicate that alkali-chloride solutions had access to the interior of the crystals along cleavage cracks and newly formed surfaces of discontinuity. This implies that armoring of the original grain by secondary depositional products did not severely restrict communication between the aqueous fluid and the unexchanged feldspar.

A similar phenomenon of solution-recrystallization was observed for isotopic experiments that involved the reaction of carbonates with aqueous chloride solutions or pure water (O'Neil et al., 1969; Northrop and Clayton, 1966; Anderson and Chai, 1974), paragonite with KCl solutions (O'Neil and Taylor, 1969), quartz with NaF solutions (Clayton et al., 1972), and barite with NaCl or NaCl plus  $H_2SO_4$  solutions (Kusakabe and Robinson, 1977). These experiments and those involving recrystallization of feldspars were not designed specifically to measure rates of isotopic exchange. Mineralogic and x-ray diffraction data obtained from these experiments suggest that any kinetic theory developed to quantify rates of isotopic exchange in systems undergoing mineralogic change must account for the surface-exchange phenomenon.

This study was undertaken to develop a basis for oxygen or hydrogen isotopic reaction kinetics that is consistent with a model of surface dissolution-precipitation. The simplified differential rate equation that is derived indicates the rate of isotopic exchange to be proportional to the degree of isotopic equilibrium and the product of the number of moles of oxygen (hydrogen) in water and the mineral, and

inversely proportional to the surface area of the mineral, the total number of moles of oxygen (hydrogen) in the system (water plus mineral) and time. Estimates of oxygen isotopic rate constants are made for a variety of experimental mineral-fluid systems (e.g., feldspar-fluid, calcite-fluid), where dissolution-reprecipitation reactions were observed. The estimation of hydrogen isotopic rate constants will be addressed in the next paper of this series. The principal difficulty in using data from the literature is that in no case was the surface area measured for either reactants or products. Therefore, surface areas used in the calculations are only estimates based on assumed grain geometries.

In addition, a detailed examination is made into factors that control diffusional isotopic exchange. In previous studies (e.g., Gilletti et al., 1978), the rate of isotopic equilibration of oxygen (or oxygen-bearing species) diffusing from a fluid into a particular phase was modeled for systems where only temperature and grain size were considered. It can be shown from a rigorous treatment of diffusion of a solute into a solid, that regardless of grain geometry the magnitude of the volume of solution to volume of solid ratio also contributes to the rate of equilibration (see Crank, 1975). According to Crank (1975) this volume ratio must be corrected for the equilibrium partition of the exchanging species between fluid and solid in terms of concentration. Diffusion equations are given for various grain geometries that demonstrate these relations.

Finally, the equations derived for both diffusion and surface-

isotopic exchange are used to compute the change in the degree of isotopic equilibration ( $F$ ) with time for systems of specified temperatures, water/mineral mass ratios and grain sizes. The water/mineral volume ratios used originally in the diffusion equations are easily converted to mass ratios if the density of both the solution and solid are known. Similarly, if density and grain geometry are known, the isotopic rate equation for surface exchange can be recast to incorporate water/mineral mass ratios rather than concentrations. These manipulations facilitate a more direct comparison of the two mechanisms for similarly defined systems. This comparison is used to illustrate how isotopic exchange can occur in various natural environments (e.g., geothermal, ore deposit, metamorphic).

## NOMENCLATURE

A	interfacial area (m <sup>2</sup> )
A'	pre-exponential term in Arrhenius equation
(C <sub>n</sub> ) <sub>j</sub>	concentration of n isotope ( <sup>18</sup> O, <sup>16</sup> O, D, H) of the jth phase (water, solid)
C <sub>0</sub>	initial concentration of solute (oxygen or oxygen-bearing species) prior to diffusion into solid
D	diffusion coefficient (cm <sup>2</sup> sec <sup>-1</sup> )
E <sub>act</sub>	activation energy (Kcal mol <sup>-1</sup> )
F	fractional approach to isotopic equilibrium
K	equilibrium constant for dissociation reaction
K'	equilibrium isotope partition ratio between solid and water corrected for concentration
M <sub>s</sub>	mass of solid in experimental run (gm)
N	number of grains comprising reactant
R	gas constant (1.987 cal mol <sup>-1</sup> K <sup>-1</sup> )
S <sub>1</sub>	number of atoms of <sup>16</sup> O(H) in solid
S <sub>2</sub>	number of atoms of <sup>18</sup> O(D) in solid
S	number of moles of oxygen (hydrogen) in solid
T	temperature (K)
V <sub>s</sub>	volume of solid (1.333πa <sup>3</sup> for sphere, bwh for plate; cc)
V <sub>w</sub>	volume of water (cc)
W	number of moles of oxygen (hydrogen) in water
W <sub>1</sub>	number of atoms of <sup>16</sup> O(H) in water
W <sub>2</sub>	number of atoms of <sup>18</sup> O(D) in water
(W/S)	mole ratio of oxygen (hydrogen) in water to that in solid

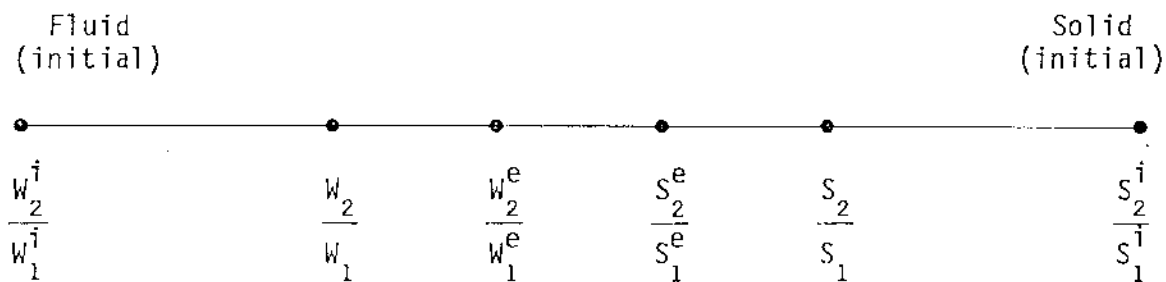


$(W/S)_m$	mass ratio of water to solid
$X_s$	total number of moles of oxygen in solid
a	radius of spherical grain or sheet (cm)
b	base; the edge of an octagonal plate or the long dimension of a rhomb (cm)
e	superscript signifying equilibrium
h	height; radius of an octagonal plate or height of a rhomb (cm)
i	superscript signifying initial
$k_+$	dissolution rate constant (moles $m^{-2}sec^{-1}$ )
$k_-$	precipitation rate constant (moles $m^{-2}sec^{-1}$ )
$g_n$	non-zero roots used in Laplace transform
$r_1$	isotopic rate constant of the forward reaction (moles $m^{-2}sec^{-1}$ )
$r_2$	isotopic rate constant of the reverse reaction (moles $m^{-2}sec^{-1}$ )
t	time (sec)
w	plate or rhomb thickness (cm)
1	subscript signifying $^{16}O(H)$
2	subscript signifying $^{18}O(D)$
$\alpha_{sw}$	isotopic fractionation factor between solid and water
$\beta$	volume of water to volume of solid ratio
$\rho$	density (gm $cc^{-1}$ )
$\delta^{18}O$	$= [(^{18}O/^{16}O)_j - (^{18}O/^{16}O)_{std} / (^{18}O/^{16}O)_{std}] 10^3$ in ‰

## DERIVATION OF AN ISOTOPIC RATE MODEL

In order to quantify the rates of isotopic exchange during dissolution-reprecipitation, a model is developed to describe the kinetics of mineral-fluid interaction which are applicable to isotopic exchange at any fluid-solid interface. Because an isotopic exchange reaction is a chemical reaction in which atoms of a given element interchange between two or more chemical forms of the element, any calculation of the rate of isotopic exchange has to make use of a general theory of reaction rates. The absolute reaction rate theory as presented, for instance, by Glasstone et al. (1941) has proved useful for this purpose. Its limitation in practical cases, such as mineral hydrolysis or reprecipitation, lies in our incomplete knowledge of the actual transition states involved and the difficulty at present of making quantum-mechanical calculations accurate enough for any but the simplest systems. For a detailed discussion of the application of transition state theory to the kinetics of mineral hydrolysis refer to Aagaard (1979).

The isotopic relationships for fluid-mineral interaction important in the development of a kinetic model are given in the following schematic bar graph



where the isotopic ratios  $(W_2^i/W_1^i)$  and  $(S_2^i/S_1^i)$  represent the initial isotopic composition of the fluid and solid, respectively; the ratios  $(W_2/W_1)$  and  $(S_2/S_1)$  refer to compositions of fluid and solid observed at some time (t) during the reaction and  $(W_2^e/W_1^e)$  and  $(S_2^e/S_1^e)$  are the equilibrium isotopic ratios of fluid and solid, respectively.

Because the number of atoms of  $^{16}\text{O}(\text{H})$  is much greater than the number of  $^{18}\text{O}(\text{D})$  atoms in water and solid (e.g., silicates, carbonates, sulfates), we can assume that

$$W_1^i \approx W_2 \approx W_1^e \quad (\approx W = W_1 + W_2) \quad (1)$$

and

$$S_1^i \approx S_2 \approx S_1^e \quad (\approx S = S_1 + S_2) \quad (2)$$

Therefore, the isotopic composition of the system can be shown as

$$\left(\frac{^{18}\text{O}}{^{16}\text{O}}\right)_{\text{sys}} = \frac{S_2^i + W_2^i}{S_1^i + W_1^i} = \frac{S_2 + W_2}{S_1 + W_1} = \frac{S_2^e + W_2^e}{S_1^e + W_1^e} \quad (3)$$

with

$$S_2 + W_2 = S_2^e + W_2^e \quad (4)$$

The equation for the oxygen (hydrogen) isotopic exchange reaction between solid and fluid can be written as

$$S_2 + W_1 \begin{matrix} r_1 \\ \rightleftharpoons \\ r_2 \end{matrix} S_1 + W_2 \quad (5)$$

where  $r_1$  and  $r_2$  are the rate constants of the forward and reverse reactions, respectively. If the rate-limiting step is the removal of oxygen (hydrogen) atoms from the surface of the solid, then the rate of change in the concentration of  $W_2$  in reaction (5) at time  $t$  can be expressed as

$$\frac{dW_2}{dt} = r_1 A (C_2)_s (C_1)_w - r_2 A (C_1)_s (C_2)_w \quad (6)$$

The parameter,  $A$ , is the total surface area of the solid phase in  $m^2$  for the system. From the following identities,

$$(C_2)_s = \frac{S_2}{S_1 + S_2} = \frac{S_2}{S} \quad (7)$$

$$(C_1)_s = \frac{S_1}{S} \quad (8)$$

$$(C_2)_w = \frac{W_2}{W} \quad (9)$$

$$(C_1)_w = \frac{W_1}{W} \quad (10)$$

substitution into equation (6) gives

$$\frac{dW_2}{dt} = A \left[ r_1 \left[ \frac{S_2}{S} \frac{W_1}{W} - r_2 \frac{S_1}{S} \frac{W_2}{W} \right] \right] \quad (11)$$

which simplifies to

$$\frac{dW_2}{dt} = \frac{A}{SW} (r_1 S_2 W_1 - r_2 S_1 W_2) \quad (12)$$

By recalling the definition of the equilibrium fractionation factor between solid and fluid as

or 
$$\alpha_{SW} = \frac{r_2}{r_1} \quad (13)$$

$$\alpha_{SW} r_1 = r_2 \quad (14)$$

and substituting equation (14) into equation (12), the following is given

$$\frac{dW_2}{dt} = \frac{Ar_1}{SW} (S_2 W_1 - \alpha_{SW} S_1 W_2) \quad (15)$$

From equation (4)

$$S_2 = S_2^e + W_2^e - W_2 \quad (16)$$

which can be used in equation (15) to yield

$$\frac{dW_2}{dt} = \frac{Ar_1}{SW} \left[ W_1 (S_2^e + W_2^e - W_2) - \alpha_{SW} W_2 S_1 \right] \quad (17)$$

or

$$\frac{dW_2}{dt} = \frac{Ar_1}{SW} \left[ W_1 (W_2^e - W_2) + W_1 S_2^e - \alpha_{SW} W_2 S_1 \right] \quad (18)$$

Rewriting the equilibrium fractionation factor,  $\alpha_{SW}$ , in the form

$$\alpha_{SW} = \left( \frac{S_2^e/S_1^e}{W_2^e/W_1^e} \right) = \left( \frac{S_2^e/S_1}{W_2^e/W_1} \right) \quad (19)$$

or

$$W_1 S_2^e = \alpha_{SW} S_1 W_2^e \quad (20)$$

equation (18) can be recast into

$$\frac{dW_2}{dt} = \frac{Ar_1}{SW} \left[ W_1 (W_2^e + W_2) + \alpha_{SW} S_1 W_2^e - \alpha_{SW} W_2 S_1 \right] \quad (21)$$

which reduces to

$$\frac{dW_2}{dt} = \frac{Ar_1}{SW} (W_2^e - W_2)(W_1 + \alpha_{SW}S_1) \quad (22)$$

Rearranging equation (22), we get

$$\frac{dW_2}{(W_2^e - W_2)} = \frac{Ar_1}{SW} (W_1 + \alpha_{SW}S_1) dt \quad (23)$$

The integrated form of equation (23) is

$$-\ln(W_2^e - W_2) = \frac{Ar_1}{SW} (W_1 + \alpha_{SW}S_1)t + \text{constant} \quad (24)$$

The integration constant can be evaluated at  $t=0$  when  $W_2 = W_2^i$  (the initial value prior to reaction)

$$\text{constant} = -\ln(W_2^e - W_2^i) \quad (25)$$

Substituting (25) into equation (24) and rearranging yields

$$\frac{r_1 t A}{SW} = -\frac{1}{(W_1 + \alpha_{SW}S_1)} \ln \left[ \frac{(W_2^e - W_2^i) - (W_2 - W_2^i)}{(W_2^e - W_2^i)} \right] \quad (26)$$

which simplifies to

$$\frac{r_1 t A}{SW} = -\frac{1}{(W_2 + \alpha_{SW}S_1)} \ln \left[ 1 - \frac{(W_2 - W_2^i)}{(W_2^e - W_2^i)} \right] \quad (27)$$

By definition

$$F = \frac{(W_2 - W_2^i)}{(W_2^e - W_2^i)} \quad (28)$$

and is the fraction of isotopic exchange, which can be substituted into equation (27) to give

$$\frac{r_1 t A}{S W} = - \frac{1}{(W_1 + \alpha_{SW} S_1)} \ln(1-F) \quad (29)$$

In this equation, (1-F) is a measure of the departure from equilibrium. Note that when F=0, there has been no exchange ( $W_2 = W_2^i$ ) and at equilibrium ( $W_2 = W_2^e$ ), or 100% exchange, F=1.

As a first approximation, we can assume that  $\alpha_{SW}$  is essentially equal to one and  $W_1 + S_1 \approx W + S$ . Then equation (29) simplifies to

$$\frac{r_1 t A}{S W} = - \frac{1}{(W+S)} \ln(1-F) \quad (30)$$

Solving for the rate constant we get

$$r_1 = \frac{-\ln(1-F)(SW)}{(W+S)tA} \quad (31)$$

where  $r_1$  is expressed as mole  $m^{-2}sec^{-1}$ . In order to determine rate constants from experiments, the surface area of the solid, moles of oxygen (or hydrogen) in solution and solid and the fraction of isotopic exchange at some time t must be known.

Once the isotopic rate constants at various temperatures are derived from equation (31) for a given dissolution-precipitation reaction, the activation energy ( $E_{act}$ ) for the reaction can be calculated from the Arrhenius equation

$$\log r_1 = \frac{-E_{act}}{2.3 RT} + \log A' \quad (32)$$

where  $A'$  is the pre-exponential factor related to some activated

complex. It apparently has little or no temperature dependence and thus can be considered a constant.

## CALCULATION OF RATE CONSTANTS FOR SELECTED EXPERIMENTAL SYSTEMS

### Problems and assumptions

Values of  $r_1$  are estimated for selected oxygen isotopic exchange experiments described in the literature using equation (31). In order to use this equation effectively, data on isotopic concentrations versus time are required from systems where P, T, A, W, S and reaction products are known. Most isotopic exchange experiments described for mineral-fluid systems exhibiting redeposition measured equilibrium isotopic fractionation factors ( $\alpha_{sw}$ ), not rates of exchange. In no case was the isotopic concentration monitored through time nor the surface area of reactants measured. In addition, the masses of solid and fluid used in each experimental run are not given, but instead described only in general terms (i.e., a typical run charge consisted of 10 mg of solid, 100 mg of solution).

Of the remaining parameters required for the use of equation (31), data on the fraction of exchange (F), time (t) and temperature are usually documented in detail. The presence of a secondary run product or recrystallized reactant has been verified by either x-ray or microscopic examination for most oxygen isotopic experiments not designed to measure diffusion coefficients.

Various assumptions are made that permit the application of the isotopic rate equation (31) to a wide spectrum of literature results.



(1) We can assume for the sake of comparison that all partial isotopic exchange observed in experiments that did not specifically address diffusion resulted from redeposition or recrystallization-type reactions. This assumption is most applicable to experiments where the technique of partial oxygen isotopic exchange was employed to estimate equilibrium fractionation factors (e.g., O'Neil and Taylor; 1967, 1969). Oxygen isotopic exchange by means of diffusion in silicates and oxides is evaluated in a later section and compared to rates computed from equation (31).

(2) In order to use equation (31), the moles of oxygen (or hydrogen) in the solution (W) and solid (S) are required. Ideally, the mass of solution and solid are known for each experimental run from which the number of moles of oxygen or hydrogen can be computed. With the exception of the study by Kulla (1979), run conditions for individual experiments are not given. Instead, an average mass of solution and solid are described, from which the moles of oxygen (or hydrogen) have been calculated.

(3) As indicated previously, surface areas of reactants have not been measured in any of the isotopic exchange experiments described in the literature. Typically, argon or nitrogen BET measurements are used as standard techniques for determining the relative surface areas of solids. These techniques generally give higher values for the surface areas than would be calculated from geometrical considerations of individual grains because the gas adsorption measurements are sensitive to surface roughness and porosity (Rimstidt, 1980). Surface

areas used in the calculation of rates of isotopic exchange are estimated from the following formulas assuming certain grain geometries.

For a sphere

$$A(m^2) = (4\pi a^2) \left( \frac{Ms}{\rho \cdot 1.33\pi a^3} \right) 10^4 \quad (33)$$

where the first term within the brackets gives the area of one sphere of radius (a) in cm and the second term computes the number of grains. The values of (a) are either taken directly from grain sizes given in each paper or estimated from the average sieve size used, where (a) equals one half of the sieve opening dimension. A spherical model is adopted for all feldspar, quartz, glass, barite, epidote, zoisite, amphibole and mica experiments unless other geometries are documented.

For a rhombohedron

$$A(m^2) = (bh) \left( \frac{Ms}{\rho \cdot bhw} \right) 10^4 \quad (34)$$

It is assumed for rhombohedron grains that (b), the base, equals the average sieving opening dimension, (h) the height equals 0.65b and the width (w) equals 0.5(b). Although these proportions are somewhat arbitrary, they are based on the shape of a typical Iceland spar calcite rhomb.

For an octagonal plate

$$A(m^2) = (4bh) \left( \frac{Ms}{\rho \cdot 4bhw} \right) 10^4 \quad (35)$$

where the height (h) equals one half of the sieve opening dimension, the base (b) equals approximately 0.8h and the width (w) equals 0.1b. These proportions are based, in part, on the description of

muscovite and paragonite run material (O'Neil and Taylor, 1969) and clay reactants described by O'Neil and Kharaka (1976). This model was used for clays and other phyllosilicates if reactants or products were described in detail. Otherwise, a spherical grain geometry was employed. The difference in surface areas computed for a given experiment using the various models averaged less than 5%.

(4) The fraction of isotopic exchange (F) given for each set of experimental runs was used directly in the rate equation (31). No attempt is made to verify the level of precision or accuracy attained in these experiments.

(5) Finally, in order to test the validity of equation (31), it is necessary to obtain data on isotopic concentration versus time as the mineral-fluid interaction proceeds. With the exception of a study on isotopic redistribution during calcite recrystallization by Anderson and Chai (1974), experimental data of this type are lacking in the literature. The determination of isotopic rate constants for a recrystallization process is illustrated with data from experiments conducted by Anderson and Chai (1974) at 305, 400 and 500°C (Fig. 1).

By recasting equation (31) to solve for t

$$t = \frac{-\ln(1-F)}{r_1} \frac{WS}{(W+S)A} \quad (36)$$

we see that it is a linear equation of the form  $y = mx$ , where  $m = -WS/r_1(W+S)A$  and  $x = \ln(1-F)$ . Therefore, if  $\ln(1-F)$  is plotted versus elapsed time and  $WS/(W+S)A$  is constant, the slope of the line will be  $-1/r_1$ . Unfortunately, Anderson and Chai (1974) did not sample the

same experiment through time, but instead conducted individual experiments at the same temperature for different durations. In addition, the grain sizes they employed varied from one run to another. Consequently, individual rate constants are calculated from equation (31) for each capsule run for all of their experiments. This same approach is adopted for all other literature results. The only reliable check we have on the validity of this approach is if we compute similar rate constants for experiments with different run conditions (i.e., different W, S, A, t, F), but where run products are chemically and mineralogically similar.

For a summary of run conditions and parameters used in equation (31), see Table 1. In cases where it was not clear whether recrystallization or deposition actually took place, the proposed product phase is bracketed with parentheses.

#### $^{18}\text{O}/^{16}\text{O}$ rates of exchange between mineral and fluid

The oxygen isotopic rate constants calculated from equation (31) for most mineral-fluid experiments described in Table 1 have been plotted on Arrhenius plots (Fig. 2 and 3). Each rate value given in these plots represents an individual run or group of runs for which a fraction of isotopic exchange was determined. From equation (32), it can be seen that the result should be a linear function if the reaction mechanism is unchanged over the temperature range of interest. Straight lines have been regressed through the data for each individual reaction (e.g., Albite + 3M KCl = Kspar + 3M NaCl) in the form

$$\log r_1 = a(10^3/T) - b \quad (37)$$

where  $a$  is the slope of the line and  $b$  is the intercept. From the slopes of these lines,  $a = (-E_{act}/R)$ , the activation energies for oxygen isotopic exchange controlled by recrystallization or deposition reactions are calculated. Table 3 summarizes the various reactions, equations for the regression lines, the regression coefficients and the activation energies for oxygen isotopic exchange.

Lines fit to feldspar-salt solution data (Fig. 2a) derived from O'Neil and Taylor (1967) indicate that below about 500°C, the rates of oxygen isotopic exchange accompanying new mineral growth resulting from Na-K ion exchange (i.e., Kspar after albite or albite after sanidine) are indistinguishable. Conversion of celsian ( $BaAl_2Si_2O_8$ ) to anorthite resulted in rate constants for isotopic exchange that are approximately one order of magnitude lower than the other feldspar-salt solution reactions. Sanidine and albite reacted with either pure water or a salt solution in equilibrium with the crystals (Fig. 2b) resulted in rate constants generally one order of magnitude lower than those calculated for feldspar-salt solution experiments. Activation energies range from 17.5 to 25.6 and 17.2 and 21.2 kcal mol<sup>-1</sup> for feldspar-salt solution and feldspar-pure water isotopic exchange, respectively.

O'Neil and Taylor (1967) defend the concept that some dissolution-redeposition occurred in their feldspar-pure water runs. No mineralogic evidence was obtained, however, to substantiate this claim. Whether the total fraction of oxygen isotopic exchange can be contributed entirely to such a process is still uncertain. It is

possible that volume diffusion of an oxygen-bearing species into the feldspars also contributed to the observed isotopic exchange.

Interestingly, rate constants computed from albite-pure water data given by Matsuhisa et al. (1979) plot virtually on top of the rate constants estimated from the O'Neil and Taylor (1967) albite-pure water data, even though the former set of experiments were conducted at 15kb and the later only at 1kb. Yund and Anderson (1978) demonstrated convincingly that oxygen diffusion coefficients have a positive dependence on fluid pressure. A similar relationship between fluid pressure and oxygen diffusion was documented by Castle and Surman (1969) in their study of magnetite. If diffusion was the principal mechanism involved in albite-pure water isotopic exchange, the relationships observed in Fig. 2b should not occur. Consequently, dissolution-reprecipitation is probably the dominate mechanism controlling oxygen isotopic exchange in the feldspar-pure water experiments, as well as the feldspar-salt solution runs.

Quartz-pure water and quartz-NaF rate constants are shown in Fig. 2c. In the quartz-NaF experiments (dashed lines), Clayton et al. (1972) observed extensive recrystallization of quartz. The separation of rate constants derived from the Clayton et al. (1972) experiments into two populations (Fig. 2c) has apparently resulted from the use of different types of quartz starting materials. Other than their oxygen isotopic composition, the exact nature of the differences between the various quartz materials, such as surface roughness, dislocations or fractures, is not known.

Rate constants derived from the quartz-pure water data of Matsuhisa et al. (1979) plot very close to the upper quartz-NaF rate line (Fig. 2c). The quartz-pure water rate constant calculated from data given by Clayton et al. (1972) is approximately one order of magnitude lower than similar rate constants computed from the Matsuhisa et al. (1979) data. Experiments by Clayton et al. (1972) were carried out at 1kb, whereas Matsuhisa et al. (1979) conducted their experiments at 2 and 15kb. The difference in the rate constants calculated for quartz-pure water isotopic exchange might be explained by the 14kb pressure difference between the two data sets if diffusion was the dominate mechanism, and not recrystallization. However, the fact that the 2kb, 700°C run of Matsuhisa et al. (1979) yields a rate constant similar to the 15kb, 700°C experiment and, at the same time plots on the upper quartz-NaF regression line, suggests that recrystallization, not diffusion, is probably the dominate mechanism. The lower rate constant for quartz-pure water derived from the data of Clayton et al. (1972) can probably be attributed to starting material variations discussed above.

The activation energies calculated for quartz-pure water and quartz-NaF oxygen isotopic exchange are approximately 10.8 and 5.4 kcal mol<sup>-1</sup>, respectively.

Rate constants for paragonite-salt solution and kaolinite-NaCl oxygen isotopic exchange are plotted in Fig. 2d. Extensive redeposition was observed in both of these sets of experiments (i.e., muscovite from paragonite, diasporite plus pyrophyllite from kaolin-

ite). In one case, paragonite was recrystallized from muscovite reacted with 3M NaCl at 500°C. The rate constant for this experiment is nearly identical to that obtained for the paragonite-3M KCl run at 500°C. These data suggest that oxygen isotopic exchange accompanying Na-K ion exchange in micas can be modeled from the line fit to these data, which yields an activation energy of 14.8 kcal mol<sup>-1</sup>.

Experiments involving kaolinite alteration to diaspore plus pyrophyllite yield isotopic rate constants similar in magnitude to the rate constants computed or extrapolated for mica-salt solution isotopic exchange. An activation energy of 9.8 kcal mol<sup>-1</sup> is estimated for the kaolinite reaction (Table 3).

Rate constants for oxygen isotopic exchange between carbonates and various types of solutions are given in Figs. 3a, 3b, and 3c. Calcite-pure water isotopic rate constants computed from data given by Anderson and Chai (1974) are in excellent agreement with rates predicted for oxygen isotopic exchange in the systems, calcite-NH<sub>4</sub>Cl and calcite-pure water from data given by O'Neil et al. (1969). In both series of experiments, extensive recrystallization of calcite was observed. Activation energies range from 6.3 to 10.4 kcal mol<sup>-1</sup> for experiments conducted by O'Neil et al. (1969) and Anderson and Chai (1974), respectively.

Dolomite reacted with NH<sub>4</sub>Cl resulted in the recrystallization of dolomite and the formation of minor amounts of Mg-calcite (Northrop and Clayton, 1966). The rates of isotopic exchange computed from these experiments (Fig. 3b) are nearly identical to the calcite-pure



water rate data shown in Fig. 3a. An activation energy of 10.9 kcal mol<sup>-1</sup> is calculated from these dolomite-NH<sub>4</sub>Cl data.

The rate of oxygen isotopic exchange between dolomite and pure water is approximately one order of magnitude lower than exchange between dolomite and NH<sub>4</sub>Cl solutions. As with the feldspar rate data, it is possible that a line representing the dolomite-pure water rates of oxygen isotopic exchange could lie one order of magnitude below the line defining dolomite-salt solution isotopic exchange, but with a similar slope. More experimental work is needed, however, to verify this empirical observation.

Rate constants for other carbonates, strontianite (SrCO<sub>3</sub>) and witherite (BaCO<sub>3</sub>) are summarized in Fig. 3c. Although the data are limited, the magnitude of the rate constants for oxygen isotopic exchange appear to be about one order of magnitude higher than calcite-pure water or dolomite-NH<sub>4</sub>Cl. As with these latter systems, strontianite and witherite underwent extensive recrystallization during hydrothermal interaction with NH<sub>4</sub>Cl solutions (O'Neil *et al.*, 1969). Activation energies for these isotopic reactions range from 6.4 kcal mol<sup>-1</sup> for strontianite-NH<sub>4</sub>Cl to 10.2 kcal mol<sup>-1</sup> for witherite-NH<sub>4</sub>Cl. Interestingly, one rate constant calculated for aragonite-NH<sub>4</sub>Cl isotopic exchange plots very near the line regressed through the strontianite-NH<sub>4</sub>Cl rate data. This may be explained, in part, by the fact that both strontianite and witherite have structural configurations similar to aragonite (Deer *et al.*, 1966) and could exhibit similar crystallization characteristics.

Rate constants for oxygen isotopic exchange in the systems barite-NaCl and barite-NaCl plus  $H_2SO_4$  are given in Fig. 3d. Kusakabe and Robinson (1977) noted widespread recrystallization of barite in their hydrothermal experiments. It is readily apparent that exchange rates are higher in the barite-NaCl plus  $H_2SO_4$  system. Kusakabe and Robinson (1977) attribute these higher rates of exchange to the increased solubility of barite in NaCl plus  $H_2SO_4$  solutions. At temperatures below about 200°C, the difference in rate constants between the two systems is at least one order of magnitude. This difference becomes smaller with increasing temperature because the rate lines converge.

The rate data given in Fig. 3d for each experimental system (i.e., barite-NaCl or barite-NaCl plus  $H_2SO_4$ ) can be partitioned into two populations and fit with separate regression lines. This suggests that oxygen isotopic exchange is controlled by a more complex phenomenon than simple recrystallization. It is possible that rapid recrystallization at higher temperatures (greater than 200°C) with subsequent armoring of reactant materials impedes the process of dissolution-redeposition. Consequently, transfer of material would occur by diffusion through the surface coating of newly crystallized barite.

For ease of comparison, regression lines have been fit to all the data computed from each experimental system. The activation energy for barite-NaCl isotope exchange is 13.4 kcal mol<sup>-1</sup> whereas barite-NaCl plus  $H_2SO_4$  yields a value of 9.2 kcal mol<sup>-1</sup>.

### Summary of oxygen isotopic rate constants

An Arrhenius plot of many of the experimentally determined oxygen isotopic rate lines for dissolution-redeposition is given in Fig. 4. Only those reactions that exhibited new mineral growth or recrystallization are given in this plot. A closer examination of this figure indicates that for specific temperature ranges, rates of oxygen isotopic exchange can be ranked, if we assume that similar conditions prevail for all phases (i.e. W, S, A, t). In general, the following ranking of rates is observed for temperatures between 150 and 350°C.

Strontianite  $\approx$  witherite > barite  $\geq$  calcite  $\geq$  dolomite > sanidine > quartz  $\geq$  albite > kaolinite > paragonite

Above 350°C, ranking becomes more difficult because of the convergence of many of the rate lines. Nevertheless, an approximate order can be given

witherite > strontianite > barite  $\geq$  albite > sanidine > dolomite  $\geq$  calcite  $\geq$  celsian > quartz  $\geq$  kaolinite  $\geq$  paragonite

With the exception of barite and paragonite, the decrease in rate constants exhibited by these phases follows approximately the trend in minerals of increasing tendency to concentrate  $^{18}\text{O}$  (O'Neil, 1979). In fact, the carbonates follow this scheme almost exactly. In general, these relations are observed because bonds formed by the light isotope ( $^{16}\text{O}$ ) are more readily broken than bonds involving the heavy isotope ( $^{18}\text{O}$ ). Thus, during chemical reactions, molecules bearing the light

isotope (carbonates, sulfates) will react slightly more readily than those with the heavy isotope (quartz, feldspars, clays).

Because the chemical reactions modeled isotopically in Fig. 4 involved growth of new phases at the expense of reactants or the recrystallization of reactants, isotopic exchange rates should depend on chemical rates of precipitation. Dibble and Tiller (1981) point out that interface detachment, not diffusion, is rate controlling over a wide range of measured dissolution rates. Rates of dissolution ( $k_+$ ) in  $\text{gm cm}^{-2}\text{sec}^{-1}$  for feldspars, quartz and biotite (annite) have been summarized by Norton and Taylor (1979) for temperatures ranging from about 50 to 400°C. Using these rates along with equilibrium constants for the various reactions, the rates of precipitation ( $k_-$ ) can be estimated from the following

$$\frac{k_+}{k_-} = K \quad (38)$$

$$k_- = \frac{k_+}{K} \quad (39)$$

The equilibrium constants for the dissociation of these phases are derived from Helgeson et al. (1978).

Rate constants for precipitation of K-feldspar, albite, annite and quartz recast in units of  $\text{moles m}^{-2}\text{sec}^{-1}$  are plotted in Fig. 5. It is apparent that below a temperature of approximately 200°C, the order in rates of precipitation is strikingly similar to the order of oxygen isotopic exchange described above for similar phases. Feldspars precipitate the fastest, followed by quartz and finally

annite. Unpublished data from Capuano (1977) indicate that at low temperatures (>100°C) calcite precipitation rates exceed all of these phases (e.g. at 25°C,  $k_p = 10^{5.5}$  moles  $m^{-2}sec^{-1}$ ). This lends further credence to our contention that precipitation rates are directly involved in controlling rates of experimental isotopic exchange, particularly if the rate line of carbonate precipitation has a slope similar to the other phases (see Fig. 5). There is no a priori reason, however, to believe that the rate of precipitation and rate of isotopic exchange controlled by surface exchange should be the same. Indeed, studies of natural systems exhibiting alteration have taught us that chemical equilibrium is closely approached or attained, whereas isotopic disequilibrium between solids and fluids is commonplace.

## DIFFUSION-CONTROLLED OXYGEN ISOTOPIC EXCHANGE

### Previous work and problems

Most of the experiments designed specifically to measure rates of isotopic exchange have addressed only the diffusional mechanism. These experiments can be divided into two types, hydrothermal and anhydrous. In the hydrothermal experiments, solids are reacted either with pure water (Giletti *et al.*, 1978) or a salt solution in equilibrium with the solid (Yund and Anderson, 1974). Anhydrous experiments involve the reaction of a solid with either CO<sub>2</sub> or O<sub>2</sub> gas (Muchlenbachs and Kushiro, 1974). Phases that have received the most attention are feldspars, olivine, phlogopite, quartz and magnetite. Table 3 summarizes Arrhenius relations for diffusion of oxygen or

oxygen-bearing species in silicates and oxides. For a more complete compilation of diffusion data for a variety of elements (e.g. O, Sr, Na, K) in silicates refer to Hart (1981). We will restrict any further discussion of diffusion to hydrothermal systems (e.g. feldspar-fluid, phlogopite-fluid).

In hydrothermal experiments where chemical equilibrium was established between an aqueous KCl solution and K-feldspar, Yund and Anderson (1974) concluded that volume diffusion of oxygen was the most effective process in the isotopic exchange of oxygen. The isotopic exchange process occurred only in response to difference in the chemical potential of  $^{18}\text{O}$  in the aqueous and solid phases. Further experimentation on the effect of fluid pressure on oxygen isotopic exchange between K-feldspar and 2M KCl solution (Yund and Anderson, 1978) produced diffusion coefficients with a positive dependence on fluid pressure. This is opposite from the effect predicted on the basis of oxygen volume diffusion theory. Thus, Yund and Anderson (1978) concluded that oxygen isotopic exchange resulted from diffusion of  $\text{OH}^-$  or possibly  $\text{H}_2\text{O}$  into the feldspar and not volume diffusion of oxygen.

However, an isotopic exchange mechanism based on volume diffusion of oxygen was proposed by Gilletti and Anderson (1975) and Gilletti et al. (1978) for hydrothermal experiments involving phlogopite (4% annite) and feldspars, respectively. Diffusion coefficients obtained from phlogopite-alkali salt solution experiments agreed with those obtained from phlogopite-pure water (Gilletti and Anderson, 1975). In

addition, oxygen diffusion data determined by Giletti et al. (1978) for K-feldspar-pure water experiments are in good agreement with oxygen diffusion data from K-feldspar-KCl experiments of Yund and Anderson (1974) and Merigoux (1968). The transport data for oxygen (or oxygen-bearing species?) in feldspars indicate that grains may be treated as ideal spheres when calculating diffusion coefficients (Giletti et al., 1978), whereas major oxygen transport in phlogopite occurs across mica layers, parallel to the c-axis (Giletti and Anderson, 1978).

A more detailed discussion of the mechanisms of exchange and problems in the experimental data base for diffusion is given by Norton and Taylor (1979). They believe that all of the hydrothermal experiments described in the literature (diffusion or otherwise) that address isotopic exchange are comprised of incongruent reactions. Specifically, hydrothermal reactions involving calcium-rich plagioclase ( $An_{96}$ ) and pure water at 350°C and 1kb are out of chemical, as well as isotopic equilibrium. Data plotted in Fig. 2b of Giletti et al. (1978) support this conclusion. In their figure, one can observe a rapid change in  $^{18}O/^{16}O$  ratios in plagioclase ( $An_{96}$ ) with depth to approximately 1000 Å, after which the ratios remain relatively constant (original plagioclase). This type of profile might be expected for a situation where new mineral growth has occurred in the outer  $1\mu$  of the grain. Conversely, volume or bulk-diffusion should produce a smoother, gradually curving profile as exhibited by their Fig. 2a for adularia-pure water interaction. Unfortunately, lack of

detailed SEM or x-ray diffraction data on run products precludes the possibility of verifying such contentions.

Certainly, dissolution-redeposition in angstrom-thick layers on surfaces is undoubtedly occurring in many hydrothermal experiments. Yund and Anderson (1974) observed, however, large oxygen isotopic fractions of exchange (0.10 to 0.50), but could detect no structural reordering or recrystallization in K-feldspars reacted with either pure water or KCl solutions below 700°C. Surman and Castle (1969) observed no secondary iron-oxyhydroxides or other phases in hydrothermal experiments involving magnetite and water. They did notice, however, the positive dependency of diffusion on fluid pressure also observed by Yund and Anderson (1978) for K-feldspars. Simple mass balance considerations suggest that large fractions of oxygen isotopic exchange should result from significant recrystallization or deposition, if these mechanisms are indeed controlling exchange. These observations, coupled with the close agreement between oxygen diffusion coefficients calculated from a variety of different feldspar-fluid experiments seem to support the hypothesis that diffusion of some oxygen-bearing species into solids is probably the dominate mechanism in these so called "diffusion" experiments. Therefore, we will use diffusion coefficients derived from Arrhenius relations given in Table 3 for modeling diffusion-controlled isotopic exchange in mineral-fluid systems.

#### Diffusion mathematics as applied to isotopic exchange

Diffusion is a process by which the molecules, atoms, or ions,



driven by a chemical potential gradient, move from point to point in either a single phase or between two different phases, such as a gas and liquid. When two or more isotopes of a specific element are transferred by a process of diffusion, a change in isotopic abundance ratio would be expected because of the velocity differences of isotopes of a given element. In the case of isotopic exchange during mineral-fluid interaction we need to consider a system in which isotopic fractionation occurs when a solute (oxygen-bearing species) is taken up by the solid. The rate of uptake of the solute and the subsequent isotopic exchange are governed by temperature and the size and shape of the solid.

In addition, Carman and Haul (1954) and Crank (1975) have pointed out that the volumes of solution and solid are also critical in quantifying the rate of equilibration of a given chemical component between two phases. The importance of this volume effect has heretofore been ignored in the application of diffusion coefficient data to the modeling of both hypothetical and natural mineral-fluid systems. For example, Giletti et al. (1978) demonstrated the effects of varying grain size and temperature on the degree of isotopic equilibration (F) for feldspars, but failed to address the volumes of either solution or feldspar. Because they assumed a constant isotopic composition for the fluid, the examples they give are only valid for a system where the volume solution greatly exceeds that of the feldspar (or very high water/solid mass ratio).

If, however, we consider a limited volume of solution, the

concentration of solute (oxygen-bearing species?) in the solution falls as solute enters the solid. For a solution that is well mixed, the concentration in the solution depends only on time, and is determined essentially by the condition that the total amount of solute in the system (solution plus solid) remains constant as diffusion proceeds (Crank, 1975). From a geologic perspective, it is more appropriate to consider systems where the volume of solution to volume of solid ratio is near unity, give or take an order of magnitude. This is particularly true in hydrothermal and metamorphic systems where small quantities of fluids can occur in microfractures or along grain boundaries.

The following set of equations demonstrates the interrelationships between the various parameters (e.g., temperature, grain size, shapes, volumes) that control isotopic exchange resulting from diffusion of a solute between a solution of limited volume and a solid. Let us first consider the diffusion of a solute from a well-mixed solution of limited volume into a sphere. Suppose that the sphere occupies the space,  $V_s$ , whereas the volume of the solution (excluding the space occupied by the sphere) is  $V_w$ . It is assumed that the concentration of solute in solution is always uniform and is initially  $C_0$ . The sphere is initially free from solute. The surface of the sphere adjusts to the partition of solute in the following manner

$$(C_2)_s = K'(C_2)_w(t) \quad (40)$$

where  $(C_2)_w(t)$  equals the concentration of  $^{18}O$  in the liquid at time

t, ( $C_2$ ) is the  $^{18}\text{O}$  concentration in the solid at t and  $K'$  is the equilibrium partition ratio corrected for concentration (we will return to this parameter later). The total amount of solute in the sphere after time t is expressed as a fraction (F) of the corresponding quantity after infinite time (equilibrium) by the relation given in Crank (1975).

$$F = 1 - \sum_{n=1}^{\infty} \frac{6\beta(\beta+1)e^{-Dq_n^2t/a^2}}{9 + 9\beta + q_n^2\beta^2} \quad (41)$$

where the  $q_n$ 's are the non-zero roots of

$$\tan q_n = \frac{3q_n}{3 + \beta q_n^2} \quad (42)$$

and

$$\beta = \frac{V_w}{V_s K'} \quad (43)$$

or

$$\beta = \frac{3V_w}{4\pi a^3 K'} \quad (44)$$

Because isotopic fractionation occurs during solute uptake into the solid, the fraction of isotopic exchange is equal to the fraction of solute in the solid. Expression (41) is valid for large values of t and demonstrates that the rate of isotopic exchange toward equilibrium (F) is a function of the solution to solid volume ratio ( $\beta$ ), as well as the grain radius, time and temperature, which fixes D. The roots of equation (42) are given in Table 6.1 of Crank (1975) for several

values of  $\beta$ .

If we consider a plane sheet or plate (i.e. mica, clay) suspended in a limited volume of well-mixed solution, an expression for diffusion at long times similar to equation (41) is given

$$F = 1 - \sum_{n=1}^{\infty} \frac{2\beta(1+\beta) e^{-Dq_n^2 t/w^2}}{1 + \beta + \beta^2 q_n^2} \quad (45)$$

where the  $q_n$ 's are the non-zero roots of

$$\tan q_n = -\beta q_n \quad (46)$$

and

$$\beta = \frac{V_w}{bwhK'} \quad (47)$$

Note that the form of equation (54) is nearly identical to equation (41) for a sphere except that grain radius ( $a$ ) is replaced by plate thickness ( $w$ ).

From these diffusion equations (i.e. 41, 45) it is obvious that the fraction of isotopic exchange in systems of limited solution volume is a function of the same parameters regardless of grain geometry. Once it can be established what grain geometry is best suited for a given mineral, then only the grain size, the volumes of solution and solid, and temperature are required to solve for  $F$ . For phases such as feldspars, quartz, magnetite and olivine, a spherical geometry is most appropriate. Hydrous silicates such as phlogopite, muscovite, montmorillonite, and kaolinite are best modeled from a plate geometry.

Of the parameters needed to solve for  $F$ , the one that has received the least attention is the solution to solid volume ratio ( $\beta$ ). In addition, it is not clear whether volume ratios used to model experimental systems described in the literature have been corrected by use of the equilibrium concentration partition ratio ( $K'$ ). Because diffusion involves changes in concentration over given distances, the isotopic equilibrium fractionation factor ( $\alpha_{sw}$ ) can not be substituted directly for  $K'$ . Instead,  $\alpha$  must be recast into a concentration ratio ( $K'$ ), that is estimated by taking the ratio of moles of  $^{18}O$   $cc^{-1}$  of solid to moles of  $^{18}O$   $cc^{-1}$  in solution at equilibrium. This is accomplished by selecting an arbitrary  $^{18}O/^{16}O$  ratio for the solid, calculating the number of moles of  $^{18}O$   $cc^{-1}$  based on density of the solid, using  $\alpha_{sw}$  to estimate an  $^{18}O/^{16}O$  ratio for the solution, correcting that for moles of  $^{18}O$   $cc^{-1}$  using the solution density, and finally taking the ratios of these concentrations.

Table 4 gives values of  $K'$  for a variety of mineral-water pairs for temperature between 200 and 400°C. The values at any given temperature are remarkably similar for the pairs given because the densities and moles of oxygen per gram of solid are very similar. The  $K'$  values increase with temperature principally because the density of water decreases. If the density was held constant, the  $K'$  values for a given mineral-water pair would be nearly identical. Above the critical point of water (>374°C), the critical density of water ( $\sim 0.3156$  gm  $cc^{-1}$ ) was used in the calculations. Application of  $K'$  values in the equations that solve for  $\beta$  (e.g. equation 43) results in

the conversion of  $\beta$  to a mass ratio, and hence it can be known as a corrected water/solid ratio. Therefore, if the diffusion equations given above are adhered to rigorously, the change in isotopic exchange toward equilibrium can be modeled for various temperatures, grain sizes and shapes, and water/solid ratios.

The calculation of (F) for given values of (D), (a) or (w) and (t) is readily accomplished by solving equations (41) and (45) graphically (Fig. 6a and 6b). In these figures modified form Crank (1975), the fraction of isotopic exchange is plotted against either  $\sqrt{Dt}/a^2$  for a sphere (Fig. 6a) or  $\sqrt{Dt}/w^2$  for a plate (Fig. 6b). The contours shown on these figures represent the percentage of total solute finally taken up by the solid, where

$$\% = \left( \frac{1}{1 + \beta} \right) 100 \quad (48)$$

By knowing the solution to solid volume ratio ( $\beta$ ), the diffusion coefficient (D), grain size (a or w), and grain geometry (sphere or plate), the fraction of isotopic exchange (F) can be determined for any time (t). Figs. 6a and 6b are useful only for systems where a solid is interacted with a well-mixed solution of limited volume.

#### COMPARISON OF SURFACE EXCHANGE AND DIFFUSION MODELS

##### Rate of oxygen isotopic equilibration for the surface exchange process

In a previous section, we gave an equation (36) that solved for the time required to attain a certain fraction of isotopic exchange as a function of surface area, temperature and the number of moles of oxygen in the solid and solution. Before a direct comparison can be

made with diffusion-controlled isotopic exchange modeled in Figs. 6a and 6b, the isotopic rate equation (31) for surface exchange must be modified. This can be accomplished by rearrangement of the A, W and S terms which are interrelated.

For a spherical grain, the surface area (A) can be represented by

$$A = 4\pi(a^2) \cdot N \quad (49)$$

where (a) is the average grain radius (cm) and N is the number of particles given by

$$N = \frac{3M_s}{\rho 4\pi(a)^3} \quad (50)$$

with the mass of the solid (in gm) and its density (gm cc<sup>-1</sup>) represented by M<sub>s</sub> and ρ, respectively. By converting M<sub>s</sub> to moles of oxygen and factoring, A in equation (49) is transformed to

$$A = \frac{3S}{(X_s)\rho a} \quad (51)$$

where S is the total number of moles of oxygen in the solid and X<sub>s</sub> is the average number of moles of oxygen per gram of solid. Substituting (51) into equation (31) yields

$$r_1 = \frac{-\ln(1-F)(WS)(X_s)(a)(\rho)}{3S(W+S)t} \quad (52)$$

which, upon rearrangement of terms, converts to

$$r_1 = \frac{-\ln(1-F)(W/S)(X_s)(a)(\rho)}{3(1+W/S)(t)(10^{-4})} \quad (53)$$

where (W/S) is the mole ratio of oxygen in water to solid. The term,  $10^{-4}$  is needed to convert from  $\text{cm}^2$  to  $\text{m}^2$ . By rearranging equation (53), the time required to attain a given fraction of isotopic exchange (F) can be evaluated for different temperatures, water/solid ratios and grain sizes as follows

$$t = \frac{-\ln(1-F)(W/S)(X_s)(a)(\rho)}{3(1+W/S)(r_1)(10^{-4})} \quad (54)$$

A similar expression is derived for a grain with an octagonal plate geometry

$$t = \frac{-\ln(1-F)(W/S)(X_s)(w)(\rho)}{(1+W/S)(r_1)(10^{-4})} \quad (55)$$

where the plate thickness (w) is used in place of grain radius. These two expressions (54 and 55) and the ones for diffusion of a solute into a sphere (41) or a plate (45) modeled graphically can now be used to compute the change in the fraction of isotopic exchange toward equilibrium with time for a system with a specified temperature, water/solid mass ratio, grain size and grain density.

#### Oxygen isotopic exchange in hypothetical mineral-fluid systems

In order to illustrate the differences and similarities between the surface exchange and diffusion models, we will examine the interaction of feldspars and micas with fluids. These phases are particularly important because of their ubiquitous occurrence in natural environments. In addition, most of our knowledge concerning mechanisms and rates of isotopic exchange are derived from experiments



on feldspars and micas.

The results of model calculations are graphically depicted in Figs. 7-10. Figures 7 and 8 show the fraction of isotopic exchange represented as  $\ln(1-F)$  plotted against time in years. Oxygen isotopic exchange by means of diffusion in the systems albite-water and phlogopite-water was modeled for 300 and 400°C, grain sizes of 0.01, 0.1 and 1.0 cm and varying fluid/mineral mass ratios (0.1, 1.0 and 10). Similarly, surface-controlled isotopic exchange was modeled for albite altering to K-feldspar and paragonite altering to muscovite and 300 and 400°C, with variable grain sizes and fluid/mineral mass ratios. The fluid/mineral mass ratio is readily converted to volume ratio for use in Figs. 6a and 6b or as the oxygen mole ratio used in equations (54) and (55). For example, a fluid/albite mass ratio of one is equal to an oxygen mole ratio of 1.82 or a volume ratio of 2.62. It is important to reiterate that the volume ratios used in the diffusion equations must be corrected for concentration by use of the equilibrium partition ratios ( $K'$ ) given in Table 4.

Results of the surface exchange calculations plotted in the upper portions of Figs. 7 and 8 indicate that the time required to attain a certain fraction of exchange is less for lower fluid/mineral mass ratios. For example, a 0.01 cm albite grain altered to K-feldspar at 400°C reaches 90% exchange in 0.17 years for a fluid/mineral mass ratio of 1.0, but only 0.04 years with a mass ratio of 0.1 (Fig. 7). A similar decrease in time is observed for paragonite altering to muscovite as the fluid/mineral mass ratio is decreased (Figs. 7, 8).

Because of the divergent nature of the straight lines, this difference in time continually increases with increasing fraction of exchange.

An increase in the grain size produces a similar result, where the time to achieve a given fraction of exchange increases. At a constant fluid/mineral mass ratio of 0.1, the time required to reach 50% exchange for albite reacted to K-feldspar at 300°C (Fig. 8) increases from .05 to over 32 years as a consequence of increasing the grain size from 0.01 to 1 cm. A change in grain thickness of 0.001 to 0.1 cm for paragonite reacted to muscovite at 300°C results in an increase in time to attain 50% exchange from 5 years to over 350 years, at a constant fluid/mineral mass ratio of 0.1. These increases in time corresponding to changes in the grain size are greater than the time differences resulting from increases of comparable magnitude in the fluid/mineral mass ratio.

Diffusion-controlled isotopic exchange shown in the lower portions of Figs. 7 and 8 behaves in a manner similar to surface exchange. The time required to attain a given fraction of exchange increases with an increase in either grain size or fluid/mineral mass ratio. The times for diffusion exchange, however, are several orders of magnitude slower than surface exchange. A system at 400°C with a grain radius of 0.01 cm and a fluid/mineral mass ratio of one reaches 90% exchange in about 0.17 years for albite altering to K-feldspar versus 800 years for oxygen diffusion in albite (Fig. 7c). Another significant difference is in the shape of the curves. Straight lines are produced for the surface exchange model, whereas curves exhibiting

a less rapid increase in fraction of exchange with increase in time are observed for the diffusion model. The curves calculated for diffusion do, however, mimic the straight lines for surface exchange in that they diverge with increasing time.

In dynamic geologic systems, parameters that influence isotopic exchange such as temperature and fluid/mineral mass ratios may also undergo change as the systems evolve toward equilibrium. The rate of equilibration of various mineral-fluid systems can be conveniently portrayed by expressing the time in years to achieve a certain degree of equilibrium as a function of the temperature (Fig. 9) or the fluid/mineral mass ratio (Fig. 10). Figure 8 demonstrates the obvious, that the time required to achieve equilibrium increases with decreasing temperature. This figure also shows that depending on the temperature, one phase may exchange faster than another. For example, at 400°C, albite altering to K-feldspar generally exchanges isotopes more readily than either quartz recrystallization or paragonite conversion to muscovite, under similar grain size and (W/S) conditions (Fig. 9). Below 300°C, however, quartz recrystallization and, in limited cases, paragonite alteration to muscovite approach equilibrium faster. In the case of diffusion (Fig. 9), feldspars tend to equilibrate faster than phlogopite at all temperatures for comparable grain size and (W/S) conditions.

Interestingly, Figure 10 demonstrates a characteristic common to both surface exchange and diffusion. This figure shows that as the fluid/mineral mass ratio increases the rate of change in the times

required to attain 90% exchange decreases. Therefore, the times required to attain 90% exchange at a  $(W/S) = 10^4$  is not much greater than that calculated for a  $(W/S) = 10$ . The most significant effects on time resulting from changes in fluid/mineral mass ratios are observed for values less than about 0.001. Times change quite radically in the region of  $(W/S)$  less than 0.001 as the curves approach the ordinate axis asymptotically. In general, an increase in time of approximately one order of magnitude occurs when the fluid/mineral mass ratio is increased from 0.1 to 10. This  $(W/S)$  range is thought to be typical of values exhibited by many continental hydrothermal ore deposits and metamorphic terrains (Taylor, 1979).

#### CONCLUSIONS

Isotopic exchange accompanying the interaction of minerals and fluids is controlled by one of two major mechanisms, surface exchange or diffusion. Surface exchange is controlled dominantly by dissolution-precipitation or recrystallization reactions. Diffusion, on the other hand, involves transport of an oxygen (hydrogen)-bearing species through phases either along lattice planes or crystal imperfections. Each of these mechanisms is in turn, controlled by a common set of physical and chemical parameters that we have evaluated quantitatively.

The rate constant for isotopic exchange accompanying surface reactions was shown to be proportional to the degree of equilibrium and the product of the number of moles of oxygen (or hydrogen) in solution and solid, and inversely proportional to the surface area,

the total moles of oxygen (hydrogen) in the system and time. Estimates of rate constants obtained from experimental data on oxygen isotopic exchange reactions fall between approximately  $10^{-4}$  and  $10^{-8}$  moles  $m^{-2}sec^{-1}$ , with activation energies ranging from about 8 to 22 kcal  $mol^{-1}$ . In general, oxygen isotopes are exchanged fastest by carbonates, followed by sulfates and finally silicates. The rate constants calculated for individual silicate-water systems are comparable to those determined from the bulk rock (granite, basalt) - fluid experiments of Cole (1980).

By rearranging the isotopic rate equation for surface exchange, the time required to attain a given degree of equilibrium can be evaluated as a function of grain size, grain density, grain geometry, water/solid mass ratio and rate at a particular temperature. Similarly, expressions were found that relate the diffusion coefficient, grain size, grain geometry, water/solid mass ratio and time to the fraction of isotopic exchange resulting from diffusion. Calculations using the surface exchange and diffusion equations indicate that the time required to attain isotopic equilibrium increases with an increase in either the water/solid mass ratio and/or grain size, or a decrease in temperature. The principal difference being, however, that rates of exchange involving surface reactions are orders of magnitude faster than isotopic exchange accompanying diffusion.

The calculations discussed above demonstrate that systems experiencing surface-controlled isotopic exchange reach equilibrium well before diffusion-controlled isotopic exchange can become a

significant contributor. The extent to which surface alteration influences the overall isotopic exchange of a solid depends on the abundance of the reaction product(s) and its mineralogy (Cole, 1980). In situations where alteration of a solid is not complete, the remaining isotopic exchange is accomplished by diffusion of an oxygen-bearing species into the unaltered portion of the grain. Final isotopic equilibrium may be achieved in periods as short as a few months for phases altered completely to secondary minerals, or in excess of  $10^6$  years for systems exchanging entirely by diffusion. As long as both processes are not in competition, systems influenced by both should exhibit equilibration times similar to the slower process, diffusion.

The significant difference in rates of equilibration observed between the two mechanisms suggests that they may be mutually exclusive in natural systems. For example, oxygen isotopic shifts observed in hydrothermal ore deposit and geothermal systems have been shown to be the result of alteration reactions during rock-water interaction (Taylor, 1979). In higher temperature igneous and metamorphic systems, isotopic exchange resulting from initial crystallization of phases is commonly erased by later retrograde processes dominated by diffusion of oxygen-bearing species from thin fluid films into solids (Bottinga and Javoy, 1975). In lower temperature environments ( $<100^\circ\text{C}$ ), Yeh and Savin (1976) attributed partial oxygen isotopic exchange between clays and seawater to crystallization reactions, whereas Lawrence and Kas<sup>t</sup>ner (1975)

demonstrated that oxygen isotopic exchange observed in detrital feldspars contained in carbonates resulted from diffusion.

Application of surface exchange and diffusion equations to well-studied geologic systems should prove useful in quantifying either time or water/solid mass ratios regardless of the degree of equilibrium. These estimates can then be tested by more rigorous mass transfer and fluid flow modeling.

Table 1. Summary of run conditions used for oxygen isotopic exchange experiments described in the literature.

Source (a)	Temperature Range (°C)	Reactants		Products (b)	Weights		Average Particle Size Range (cm) (c)	Average WS/W+S (d)	Average A(m <sup>2</sup> ) (e)	Time Range (sec)
		Solid	Solution		Solid (gm)	Solution (gm)				
O/T67	420-300	Celsian	2m CaCl <sub>2</sub>	Anorthite	0.025	0.2	0.00075	5.08 × 10 <sup>-4</sup>	0.00308	4.3 × 10 <sup>5</sup> - 3.78 × 10 <sup>6</sup>
O/T67	600	Glass-An	H <sub>2</sub> O	Anorthite	0.025	0.2	0.0025	6.75 × 10 <sup>-4</sup>	0.00362	2.77 × 10 <sup>5</sup> - 5.18 × 10 <sup>5</sup>
O/T67	350-300	Sanidine	2-3m NaCl	Albite	0.025	0.2	0.00075 - 0.0055	6.75 × 10 <sup>-4</sup>	5.3 - 39.1 × 10 <sup>-4</sup>	7.92 × 10 <sup>4</sup> - 1.89 × 10 <sup>6</sup>
O/T57	350-550	Albite	3m KCl	K-feldspar	0.025	0.2	0.0025 - 0.0113	7.14 × 10 <sup>-4</sup>	5.2 - 11.4 × 10 <sup>-4</sup>	3.6 × 10 <sup>3</sup> - 4.03 × 10 <sup>6</sup>
O/T67	500-800	Sanidine	H <sub>2</sub> O	(Sanidine)	0.025	0.2	0.00075 - 0.0055	6.75 × 10 <sup>-4</sup>	5.3 - 39.1 × 10 <sup>-4</sup>	1.72 × 10 <sup>5</sup> - 5.36 × 10 <sup>5</sup>
O/T67	585-550	Albite	H <sub>2</sub> O	(Albite)	0.025	0.2	0.0025	7.14 × 10 <sup>-4</sup>	1.145 × 10 <sup>-3</sup>	2.23 × 10 <sup>5</sup>
O/T59	350-500	Paragonite	3M KCl	Muscovite	0.025	0.2	(30 × 24 × 2.4) × 10 <sup>-6</sup>	7.33 × 10 <sup>-4</sup>	0.0914	1.58 × 10 <sup>5</sup> - 4.03 × 10 <sup>6</sup>
C/O/M	195-500	Quartz	0.7m NaF	Quartz	0.0225	0.2	2.5 × 10 <sup>-5</sup>	7.02 × 10 <sup>-4</sup>	0.1019	8.6 × 10 <sup>4</sup> - 4.31 × 10 <sup>6</sup>
M/G/C	400-700	Quartz	H <sub>2</sub> O	(Quartz)	0.01	0.0058	0.0001	1.63 × 10 <sup>-4</sup>	0.01132	4.32 × 10 <sup>5</sup> - 1.21 × 10 <sup>6</sup>
M/G/C	400-700	Albite	H <sub>2</sub> O	(Albite)	0.01	0.0058	0.0001	1.56 × 10 <sup>-4</sup>	0.01145	1.72 × 10 <sup>5</sup> - 6.05 × 10 <sup>5</sup>
C/A	305-700	Calcite	H <sub>2</sub> O	Calcite	0.035	0.2	(19 × 9.5 × 12) × 10 <sup>-4</sup>	9.59 × 10 <sup>-4</sup>	0.00133	3.96 × 10 <sup>4</sup> - 4.0 × 10 <sup>6</sup>
O/C/M	197-493	Calcite	H <sub>2</sub> O	Calcite	0.03	0.2	(64 × 32 × 41) × 10 <sup>-5</sup>	8.3 × 10 <sup>-3</sup>	0.00345	1.22 × 10 <sup>-6</sup> - 1.6 × 10 <sup>-6</sup>
O/C/M	60-200	Strontianite	0.7m NH <sub>4</sub> Cl	Strontianite	0.03	0.2	(64 × 32 × 41) × 10 <sup>-5</sup>	5.98 × 10 <sup>-4</sup>	0.002514	1.58 × 10 <sup>5</sup> - 5.0 × 10 <sup>6</sup>
O/C/M	103-205	Witherite	0.7m NH <sub>4</sub> Cl	Witherite	0.03	0.2	(64 × 32 × 41) × 10 <sup>-5</sup>	4.38 × 10 <sup>-4</sup>	0.002175	1.58 × 10 <sup>5</sup> - 6.59 × 10 <sup>5</sup>
N/C	255-660	Dolomite	0.5m NH <sub>4</sub> Cl	Dolomite + Mg Calcite	0.025	0.21	(14 × 7 × 9) × 10 <sup>-4</sup>	7.61 × 10 <sup>-4</sup>	0.00123	3.28 × 10 <sup>5</sup> - 2.14 × 10 <sup>6</sup>
O/K	100-350	Kaolinite	0.04N NaCl	Pyrophyllite + Diaspore	0.15	0.5	(22 × 11 × 13) × 10 <sup>-4</sup>	4.4 × 10 <sup>-4</sup>	0.00536	5.7 × 10 <sup>6</sup> - 5.05 × 10 <sup>7</sup>
K	170-320	Glass-Kaol.	H <sub>2</sub> O	Kaolinite	0.05	0.15	0.001 - 0.01 ?	1.44 × 10 <sup>-3</sup>	1.15 - 11.5 × 10 <sup>-3</sup>	8.64 × 10 <sup>5</sup> - 9.24 × 10 <sup>6</sup>
K	170-320	Glass-Mont.	H <sub>2</sub> O	Mont.	0.05	0.15	0.001 - 0.01 ?	1.32 × 10 <sup>-3</sup>	1.15 - 11.5 × 10 <sup>-3</sup>	1.73 × 10 <sup>6</sup> - 6.22 × 10 <sup>6</sup>
K/R	110-350	Barite	1m H <sub>2</sub> SO <sub>4</sub> + 1m NaCl	Barite	0.2	10.0	0.0015	3.41 × 10 <sup>-3</sup>	8.94 × 10 <sup>-3</sup>	1.1 × 10 <sup>6</sup> - 1.18 × 10 <sup>7</sup>
K/R	110-350	Barite	1m NaCl	Barite	0.1	5.0	0.0015	1.70 × 10 <sup>-3</sup>	4.47 × 10 <sup>-3</sup>	1.9 × 10 <sup>6</sup> - 2.97 × 10 <sup>7</sup>



- (a) O/T67 = O'Neil and Taylor (1967); O/T69 = O'Neil and Taylor (1969); C/O/M = Clayton et al. (1972); M/G/C = Matsuhisa et al. (1979); C/A = Chai and Anderson (1974); O/C/M = O'Neil et al. (1969); N/C = Northrop and Clayton (1966); O/K = O'Neil and Kharaka (1976); K = Kulla (1979); K/R = Kusakabe and Robinson (1977).
- (b) Phases formed either as an alteration product of the reactant or as recrystallized reactant. Phases in parenthesis are for experiments where recrystallization and/or alteration were not convincingly demonstrated.
- (c) Particle sizes for feldspars, quartz, barite and ground glass are given as radii assuming a spherical geometry. Particle sizes for sheet silicates such as paragonite and kaolinite are given as the base  $\times$  width  $\times$  height assuming a octagonal plate geometry. A rhombohedral geometry is assumed for carbonates with particle sizes representing the base  $\times$  width  $\times$  height. See the text for a discussion of particle sizes and estimation of surface area.
- (d) The ratio of the product of the number of moles of oxygen in water ( $\frac{w}{S}$ ) and solid ( $\frac{S}{R}$ ) to the sum the number of moles of oxygen in the system.

Table 2. Temperature functions of the oxygen isotopic rate constants for various mineral-fluid reactions.

Reaction:	Data Source	Log r = (k)	$r_g$ (l)	Activation Energy	
				kJ/mol	kcal/mol
1. Sanidine + 3m NaCl = Albite + 3m KCl	a	-3.831(1000/T) - 0.518	-0.91	73.4	17.5
2. Sanidine + H <sub>2</sub> O = Sanidine + H <sub>2</sub> O	a	-3.767(1000/T) - 1.814	-0.88	72.2	17.2
3. Celsian + 2m CaCl <sub>2</sub> = Anorth + 2m BaCl <sub>2</sub>	a	-4.789(1000/T) - 0.231	-0.99	91.8	21.9
4. Ab + 3m KCl = Ksp + 3m NaCl	a	-5.596(1000/T) + 2.181	-0.90	107.2	25.6
5. Ab + H <sub>2</sub> O (NaCl) = Ab + H <sub>2</sub> O (NaCl)	a	-4.634(1000/T) - 1.441	-0.88	88.8	21.2
6. Parag. + 3M KCl = Musc. + 3M NaCl	b	-3.225(1000/T) - 3.684	-0.95	61.8	14.8
7. Qtz + 0.7m NaF = Qtz + 0.7m NaF	c	-1.151(1000/T) - 5.893	-0.96	22.1	5.3
8. Qtz + 0.7m NaF = Qtz + 0.7m NaF	c	-1.225(1000/T) - 6.674	-0.91	23.5	5.6
9. Qtz + H <sub>2</sub> O = Qtz + H <sub>2</sub> O (15kb)	d	-2.368(1000/T) - 4.406	-0.97	45.4	10.8
10. Ab + H <sub>2</sub> O = Ab + H <sub>2</sub> O (~12kb)	d	-4.424(1000/T) - 1.509	-0.99	84.8	20.2
11. Cc + H <sub>2</sub> O = Cc + H <sub>2</sub> O	e	-2.273(1000/T) - 3.325	-0.86	43.5	10.4
12. Cc + H <sub>2</sub> O (NH <sub>4</sub> Cl) = Cc + H <sub>2</sub> O (NH <sub>4</sub> Cl)	f	-1.375(1000/T) - 4.576	-1.0	26.3	6.3
13. Stron. + NH <sub>4</sub> Cl = Stron. + NH <sub>4</sub> Cl	f	-1.389(1000/T) - 2.992	-0.87	26.6	6.4
14. Wither. + NH <sub>4</sub> Cl = Wither. + NH <sub>4</sub> Cl	f	-2.219(1000/T) - 1.363	-0.98	42.5	10.2
15. Dol + NH <sub>4</sub> Cl = Dol + MgCc + NH <sub>4</sub> Cl	g	-2.383(1000/T) - 2.970	-0.93	45.7	10.9
16. Kaol. + 0.04N NaCl = Pyroph + Diaspore	h	-2.085(1000/T) - 5.330	-0.97	39.9	9.5
17. Kaol. Glass + H <sub>2</sub> O → Kaol. + H <sub>2</sub> O (0.01cm)	i	-1.827(1000/T) - 2.468	-0.92	35.0	8.4
18. Kaol. Glass + H <sub>2</sub> O → Kaol. + H <sub>2</sub> O (0.001cm)	i	-1.827(1000/T) - 3.468	-0.92	35.0	8.4
19. Barite + 1m NaCl + 1m H <sub>2</sub> SO <sub>4</sub> = Bar + Soln	j	-2.01 (1000/T) - 2.515	-0.97	38.5	9.2
20. Barite + 1m NaCl = Bar + Soln	j	-2.937(1000/T) - 1.323	-0.98	56.3	13.4
21. Mont. Glass + H <sub>2</sub> O → Mont. + H <sub>2</sub> O (0.01cm)	i	-3.122(1000/T) - 0.039	-0.99	59.8	14.3
22. Mont. Glass + H <sub>2</sub> O → Mont. + H <sub>2</sub> O (0.001cm)	i	-3.122(1000/T) - 1.039	-0.99	59.8	14.3

## Notes

### Data Source:

- (a) O'Neil and Taylor (1967)
- (b) O'Neil and Taylor (1969)
- (c) Clayton et al. (1972)
- (d) Matsuhisa et al. (1979)
- (e) Anderson and Chai (1974)
- (f) O'Neil et al. (1969)
- (g) Northrop and Clayton (1966)
- (h) O'Neil and Kharaka (1976)
- (i) Kulla (1979)
- (j) Kusakabe and Robinson (1977)
  
- (k) Rate constant  $r$  in moles  $\text{O m}^{-2}\text{sec}^{-1}$
- (l)  $r_g$  is the regression coefficient
  
- (m) Abbreviations: Anorth = Anorthite, Ab = Albite, Parag = Paragonite, Musc, = Muscovite, Qtz = Quartz, Cc = Calcite, Stron = Strontianite, Wither = Witherite, Dol = Dolomite, Kaol = Kaolinite, Pyroph = Pyrophyllite, Mont = Montmorillonite, Bar = Barite

Table 3. Arrhenius relations for diffusivity of oxygen or oxygen-bearing species in silicates or oxides

Phase	Temp. Range (°C)	Medium	$D(\text{cm}^2\text{sec}^{-1}) =$	Isotopic Method	Data Source
Adularia	350-601	H <sub>2</sub> O	$4.51 \times 10^{-8} \exp(-25.6/RT)$	ion-probe	a
Adularia	520-800	KCl	$9 \times 10^{-7} \exp(-32/RT)$	bulk	b
Adularia	400-700	KCl	$5.3 \times 10^{-7} \exp(-29.6/RT)$	bulk	c
Albite	440-805	NaCl	$4.5 \times 10^{-5} \exp(-37/RT)$	bulk	b
Albite	350-800	H <sub>2</sub> O	$2.31 \times 10^{-9} \exp(-21.3/RT)$	ion-probe	a
Albite	600-800	NaCl	$2.5 \times 10^{-5} \exp(-37/RT)$	bulk	d
Microcline	400-700	KCl	$2.8 \times 10^{-6} \exp(-29.6/RT)$	bulk	c
Anorthite	350-805	H <sub>2</sub> O	$1.4 \times 10^{-7} \exp(-26.2/RT)$	ion-probe	a
Phlogopite	500-800	H <sub>2</sub> O, KCl	$1 \times 10^{-9} \exp(-29/RT)$	bulk	e
Magnetite	300-600	H <sub>2</sub> O	$3.2 \times 10^{-14} \exp(-17/RT)$	bulk	f
Quartz	1000-1220	O <sub>2</sub>	$3.7 \times 10^{-9} \exp(-55/RT)$	bulk	g

- (a) Gilletti et al. (1978)
- (b) Merigoux (1968)
- (c) Yund and Anderson (1974)
- (d) Anderson and Kasper (1975)
- (e) Gilletti and Anderson (1975)
- (f) Castle and Surman (1969)
- (g) Haul and Dumbgen (1962)

Table 4. Summary of  $K'$ (a) values estimated for various mineral-water pairs

Mineral Pair (b)	$K'$				
	200°	250°	300°	350°	400°
Quartz-Water	1.86	2.01	2.25	2.79	5.06
Albite-Water	1.69	1.82	2.04	2.53	4.59
K-feld-Water	1.55	1.67	1.87	2.32	4.22
Anorthite-Water	1.66	1.80	2.01	2.50	4.54
Muscovite-Water	1.79	1.93	2.16	2.69	4.88
Calcite-Water	1.71	1.85	2.07	2.57	4.65

- (a)  $K'$  is the equilibrium oxygen isotope partition ratio between solid and water calculated in terms of concentration (see text).
- (b) Equilibrium fractionation factors used to calculate the various  $K'$  values are derived from Friedman and O'Neil (1977).

## REFERENCES

- Aagaard P. (1979) Thermodynamic and kinetic analysis of silicate hydrolysis at low temperatures and pressures. Ph.D. Thesis, University of California, Berkeley.
- Anderson T. F. and Chai B. T. H. (1974) Oxygen isotope exchange between calcite and water under hydrothermal conditions. In Geochemical Transport and Kinetics (Editors A. W. Hofmann et al.) Carnegie Inst. Washington, Publ. 634, 219-227.
- Anderson T. F. and Kasper R. B. (1975) Oxygen self-diffusion in albite under hydrothermal conditions. EOS, Trans. Am. Geophys. Union 56, 459.
- Bottinga Y. and Javoy M. (1975) Oxygen isotope partitioning among the minerals in igneous and metamorphic rocks. Rev. Geophys. Space Phys. 13, 401-418.
- Carman P. C. and Haul R. A. W. (1954) Measurement of diffusion coefficients. Proc. Roy. Soc. London 222, A, 109-118.
- Castle J. E. and Surman P. L. (1969) The self-diffusion of oxygen in magnetite. The effect of anion vacancy concentration and cation distribution. J. Phys. Chem. 73, 632-634.
- Clayton R. N., O'Neil J. R. and Mayeda T. K. (1972) Oxygen isotope exchange between quartz and water. J. Geophys. Res. 77, 3057-3067.
- Cole D. R. (1980) Mechanisms and rates of stable isotopic exchange in hydrothermal rock-water systems. Ph.D. Thesis, The Pennsylvania State University.

- Crank J. (1975) The Mathematics of Diffusion. 2nd edition, Oxford University Press.
- Deer W. A., Howie R. A. and Zussman J. (1966) An Introduction to the Rock-Forming Minerals. Longman Group Ltd.
- Friedman I. and O'Neil J. R. (1977) Compilation of stable isotope fractionation factors of geochemical interest. U.S. Geol. Surv. Prof. Pap. 440-kk.
- Giletti B. J. and Anderson T. F. (1975) Studies in diffusion - II. Oxygen in phlogopite mica. Earth Planet. Sci. Lett. 28, 225-233.
- Giletti B. J., Semet M. P. and Yund R. A. (1978) Studies in diffusion - III. Oxygen in feldspars: an ion microprobe determination. Geochim. Cosmochim. Acta 42, 45-57.
- Glasstone S., Laidler K. J. and Eyring H. (1941) The Theory of Rate Processes. McGraw-Hill, New York.
- Hart S. R. (1981) Diffusion compensation in natural silicates. Geochim. Cosmochim. Acta 45, 279-291.
- Haul R. and Dumbgen G. (1962) Investigation of oxygen diffusion in  $TiO_2$ , quartz and quartz glass by isotope exchange. Z. Elektrochem. 66, 636-641.
- Helgeson H. C., Delany J. M., Nesbitt H. W. and Bird D. K. (1978) Summary and critique of the thermodynamic properties of rock-forming minerals. Am. J. Sci. 278A.

- Kulla J. B. (1979) Oxygen and hydrogen isotopic fractionation factors determined in experimental clay-water systems. Ph.D. Thesis, University of Illinois.
- Kusakabe M. and Robinson B. W. (1977) Oxygen and sulfur isotope equilibria in the  $\text{BaSO}_4\text{-HSO}_4^-$  system from 110 to 350°C and applications. Geochim. Cosmochim. Acta 41, 1033-1040.
- Lawrence J. R. and Kastner M. (1975)  $\text{O}^{18}/\text{O}^{16}$  of feldspars in carbonate rocks. Geochim. Cosmochim. Acta 39, 97-102.
- Matsuhisa Y., Goldsmith J. R. and Clayton R. N. (1979) Oxygen isotopic fractionation in the system quartz-albite-anorthite-water. Geochim. Cosmochim. Acta 43, 1131-1140.
- Merigoux H. (1968) Etude de la mobilite de l'oxygen dans les feldspaths alcalins. Bull. Soc. Fr. Mineral. Cristallogr. 91, 51-64.
- Muehlenbachs K. and Kushiro I. (1974) Oxygen isotope exchange and equilibrium of silicates with  $\text{CO}_2$  or  $\text{O}_2$ . Carnegie Inst. Wash., Ybk. 73, 232-236.
- Northrop D. A. and Clayton R. N. (1966) Oxygen-isotope fractionations in systems containing dolomite. J. Geol. 74, 174-196.
- Norton D. and Taylor H. P. (1979) Quantitative simulation of the hydrothermal systems of crystallizing magmas on the basis of transport theory and oxygen isotope data: An analysis of the Skaergaard intrusion. J. Petrology 20, 421-486.



- O'Neil J. R. and Taylor H. P., Jr. (1967) The oxygen isotope and cation exchange chemistry of feldspars. Am. Mineralogist 52, 1414-1437.
- O'Neil J. R., Clayton R. N. and Mayeda T. K. (1969) Oxygen isotope fractionation in divalent metal carbonates. J. Chem. Phys. 51, 5547-5558.
- O'Neil J. R. and Taylor H. P., Jr. (1969) Oxygen isotope equilibrium between muscovite and water. J. Geophys. Res. 74, 6012-6022.
- O'Neil J. R. and Kharaka Y. K. (1976) Hydrogen and oxygen isotope exchange between clay minerals and waters. Geochim. Cosmochim. Acta 40, 241-246.
- Rimstidt J. D. and Barnes H. L. (1980) The kinetics of silica-water reactions. Geochim. Cosmochim. Acta 44, 1683-1699.
- Taylor H. P., Jr. (1979) Oxygen and hydrogen isotope relationships in hydrothermal mineral deposits. In Geochemistry of Hydrothermal Ore Deposits, 2nd edition (ed. H. L. Barnes). pp. 356-277. Wiley-Interscience, New York.
- Yeh H. and Savin S. M. (1976) The extent of oxygen isotope exchange between clay minerals and sea water. Geochim. Cosmochim. Acta 40, 743-748.
- Yund R. A. and Anderson T. F. (1974) Oxygen isotope exchange between potassium feldspar and KCl solution. In Geochemical Transport and Kinetics (Editors A. W. Hofmann et al.) Carnegie Inst. Washington, Publ. 634, 99-105.

Yund R. A. and Anderson T. F. (1978) The effect of fluid pressure on oxygen isotope exchange between feldspar and water. Geochim. Cosmochim. Acta 42, 235-239.

### Figure Captions

- Fig. 1.  $-\ln(1-F)$  vs elapsed time for oxygen isotopic exchange in the system, calcite-water. The data are from Anderson and Chai (1974). The slopes of the lines equal  $-WS/r(W+S)A$ .
- Fig. 2. Arrhenius plots of rate constants (moles  $m^{-2}sec^{-1}$ ) for various oxygen isotopic exchange reactions between silicates and fluids. (a) feldspars-fluid data from O'Neil and Taylor (1967): albite - 2m KCl ( $\nabla$  - long dashes), sanidine - 2m ( $\square$ ) and 3m ( $\triangle$ ) NaCl (long dashes), celsian - 2m  $CaCl_2$  ( $\diamond$  - solid line), open symbols = natural reactants, solid = synthetic reactants. (b) feldspars -  $H_2O$  data from O'Neil and Taylor (1967) for 1kb: sanidine -  $H_2O$  ( $\bullet$ ,  $\circ$  - long dashes), albite -  $H_2O$  ( $\circ$ ) and 3m NaCl ( $\triangle$ ) (short dashes), open = natural, solid = synthetic; natural albite -  $H_2O$  data (short-long dash) from Matsuhisa et al. (1979): 7kb ( $\blacktriangle$ ), 12kb ( $\bullet$ ), 15kb ( $\blacksquare$ ). (c) quart -  $H_2O$  data (solid line) at 2kb ( $\circ$ ) and 15kb ( $\bullet$ ) from Matsuhisa et al. (1979), quartz - NaF (short and short plus long dashes) at 1kb from Clayton et al. (1972). (d) paragonite - 3m KCl ( $\blacktriangledown$ ) and muscovite - 3m NaCl ( $\blacktriangle$ ) data (solid line) from O'Neil and Taylor (1969), kaolinite - 0.04N NaCl ( $\triangle$ ) data (short-long dashed line) from O'Neil and Kharaka (1976).
- Fig. 3. Arrhenius plots of rate constants (moles  $m^{-2}sec^{-1}$ ) for various oxygen isotopic exchange reactions between carbonate

or sulfates and fluids. (a) calcite -  $H_2O$  (○) and 0.7m  $NH_4Cl$  (△) from Anderson and Chai (1974)(solid line) and O'Neil et al. (1969)(long dashed line), respectively. (b) dolomite -  $H_2O$ (○),  $-NH_4Cl$  (△),  $-NH_4Cl + NH_4HCO_3$  (◇), and  $-NH_4HCO_3$  (□) data from Northrop and Clayton (1966). The solid line has been regressed through the  $H_2O$  and  $NH_4Cl$  data only. (c) strontianite - 0.7m  $NH_4Cl$  (lower solid line) (□) witherite - 0.7m  $NH_4Cl$  (upper line) (○) and aragonite - 0.7m  $NH_4Cl$  (△) data are from O'Neil et al. (1969). (d) barite - 1m NaCl (▽) and 1m  $H_2SO_4$  plus NaCl (△) data are from Kusakabe and Robinson (1977). The dashed lines have been regressed through all data points for the respective systems, whereas the solid lines have been regressed according to possible inflections in the data (see text for a discussion). Solid = synthetic and open = natural for all of Fig. 3.

Fig. 4. A composite Arrhenius plot of rate constants for oxygen isotopic exchange reactions that exhibited precipitation or recrystallization. See Table 2 in order to match the appropriate reaction given by number with the rate line.

Fig. 5. Arrhenius plot of precipitation rate constants (moles  $m^{-2} sec$ ) for various silicate-water reactions. Data were generated from dissolution values given by Norton and Taylor (1979).

Fig. 6. Fraction of isotopic exchange vs  $\sqrt{Dt/a^2}$  for a sphere (a) and  $\sqrt{Dt/w^2}$  (b) for a plate, contoured for various values of  $1/1+\beta$ . These figures have been modified from Crank (1975).

Fig. 7. Fraction of oxygen isotopic exchange given as  $-\ln(1-F)$  vs time in years for surface exchange (a, b) and diffusion (c, d) reactions in feldspars and mica-fluid systems at 400°C. Rate constants for reaction (4) and (6) given in Table 2 were used in equations (52) and (53), respectively to model albite and paragonite alteration. Diffusion coefficients from Giletti et al. (1978) and Giletti and Anderson (1975) were used to model albite and phlogopite, respectively. W/S is the oxygen mole ratio of fluid to solid, a is grain radius in cm, and w is plate thickness in cm.

Fig. 8. Fraction of oxygen isotopic exchange given as  $-\ln(1-F)$  vs time in years for surface exchange (a, b) and diffusion (c, d) reactions in feldspar and mica-fluid systems at 300°C. The rate constants and diffusion coefficients are derived from the same sources described for Fig. 7. Nomenclature is also the same as in Fig. 7.

Fig. 9. Time to 90% oxygen isotopic exchange vs temperature for (a) quartz recrystallization (reaction 7, Table 2), paragonite altering to muscovite (reaction 6, Table 2) and albite altering to K-feldspar (reaction 4, Table 2), and (b)

diffusion-controlled isotopic exchange between albite- $H_2O$  and phlogopite- $H_2O$ . Nomenclature, rate constants and diffusion coefficients are the same as described for Fig. 7.

Fig. 10. Time to 90% oxygen isotopic exchange vs water/solid mass ratio. (a) the surface exchange reactions modeled are albite to K-feldspar (reaction 4, Table 2) and sanidine altering to albite (reaction 1, Table 2), (b) diffusion modeled for albite and phlogopite. Nomenclature, rate constants and diffusion coefficients are the same as described for Fig. 7.

